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Advanced Characterization of Forms of Chlorine, Organic Sulfur, and Selected Trace Elements in Available Coals from Operating Illinois Mines

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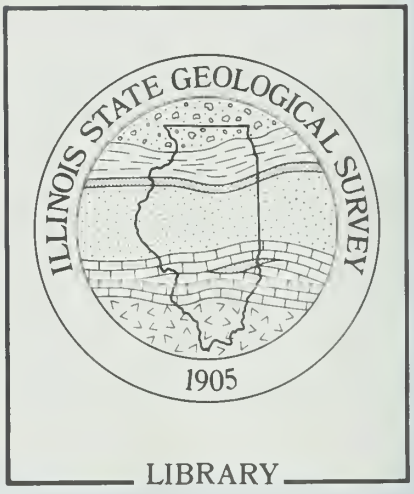

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Abstract

The presence of sulfur and chlorine (Cl) in Illinois coals has long been a major concern for their end users. About half of the sulfur in high-sulfur Illinois coals is combined into pyrite. Grinding and physical cleaning can remove most of the Cl and pyrite from coals. However, removal of organic sulfur, which generally makes up the other half of the sulfur in Illinois coal, requires that chemical bonds be broken through alteration of the coal's molecular structure. Before an integrated process of sulfur and Cl removal can be successfully developed, the fundamental associations of organic sulfur and Cl in coal must be understood in detail.

The goals of this study were (1) to use x-ray absorption near-edge spectroscopy (XANES) to examine forms of Cl and organic sulfur in as-shipped coals from Illinois mines, (2) to obtain basic data on Cl removal via froth flotation of the coals ground to fine and ultrafine particle sizes, and (3) to eval-uate the XANES method for direct assessment of the organic and inorganic affinities of trace elements in Illinois coals.

A total of 21 coal samples from five specific geographic regions of the Illinois coal field were examined. The Cl XANES spectra of the samples were very similar and showed that chloride anions were the predominant form of Cl and that thiophenic sulfur accounted for 61 to 82% of the organic sulfur in the coals. The thiophenic fraction of organic sulfur was generally greater in coal samples from the deeper parts of the Illinois Basin than in samples from the other areas.

The Cl leachability tests indicated that wet-grinding and froth flotation decreased the Cl content of most samples from regions 1, 2, and 3 by 29 to 81% and in one sample from region 4S by 60%.

The XANES analysis of selected trace metals in one sample yielded mixed results. For As and Zn, XANES results provided a definitive interpretation of their modes of occurrence; As is associated with pyrite and can be oxidized to form arsenate, and Zn occurs in a form of ZnS. For Ti, V, Cr, and Mn, a definitive interpretation was not possible.

Introduction

The Cl content of Illinois coals generally increases with the depth of the coal seam (Gluskoter and Rees 1964). As shallow deposits are depleted, future Illinois coal production is likely to come from the more deeply buried parts of the major coal seams with higher Cl contents. Published data for British coals (Reid 1971, Bettelheim et al. 1980) have correlated the corrosion of boilers at power plants with high-Cl content. Based on the British data, many U.S. boiler manufacturers have recommended a maximum Cl level of 0.3% for burning U.S. coals, but this limit decreases the market potential of high-Cl Illinois coals. Although recent U.S. studies (Doane et al. 1994; Chou et al. 1998, 2000) have indicated that the Cl in high-Cl Illinois coals is not a major cause of corrosion, until boiler manufacturers relax their Cl limits, the presence of Cl in Illinois coals remains a marketing concern.

The presence of sulfur also has long been a major concern for the end users of Illinois coals. High-sulfur Illinois coals contain significant amounts of both organic and pyritic sulfur. On average, about half of the sulfur in high-sulfur Illinois coals is combined into pyrite. The literature indicates that fine grinding and physical cleaning can remove up to 95% of the pyrite from coal and recover 80% of the heat content (Read et al. 1988, Honaker and Govindarajan 1998). The literature also indicates the possibility of removing 70% or more of the Cl from finely ground coals during leaching (Chou et al. 1991). Thus, physical cleaning may help solve the problems caused by both pyrite and Cl in coals. However, organic sulfur, which generally makes up the other half of the sulfur in Illinois coal, cannot be removed by physical coal cleaning. Removal of the organic sulfur requires that chemical bonds be broken through alteration of the coal's molecular structure. Organic sulfide (weakly bonded) ought to be more easily removed from coals than thiophenic sulfur (strongly bonded). If a mild thermal or chemical method can be found that can reduce organic forms of sulfur in coal by 50% and such a method can be combined with physical cleaning, a fuel with less than 1.5% sulfur content may be derived from a high-sulfur Illinois coal containing 4% total sulfur. For such an integrated process or other advanced coal utilization processes to be successfully developed, the fundamental associations of organic sulfur and Cl in coal must be understood.

The current ASTM methods (ASTM 2000) can determine the total Cl content, but not the forms of Cl in coal. Previous British attempts (Edgcombe 1956, Daybell and Pringle 1958, Gibb 1983) and some U.S. studies (Cox 1984, 1985) on analyses of Cl in coal by indirect methods suggested that Cl in coal exists primarily in the form of dissolved salts. Based on the different chemical reactivity of organic and inorganic chloride, Hamling and Kaegi (1984) reported that Cl in coal samples from one of the high-Cl Illinois mines was predominantly in the form of organic chloride(s) and that the organically associated Cl apparently did not contribute to boiler corrosion and fouling problems. Demir et al. (1990) and Chou (1991) concluded that most of the Cl in Illinois coals is present as exchangeable anions adsorbed on the inner surfaces of micropores in the macerals, and dissolved salt accounts for only a small portion of the total Cl. The discrepancies between these findings suggested the need for obtaining representative data on forms of Cl in coal with a direct method of determination.

As with Cl analysis, the current standard methods for sulfur analysis in coal are based on ASTM procedures

(ASTM 2000). These methods are adequate for analyzing total, pyritic, and sulfatic sulfur in coal, but they do not provide a direct measurement of total organic sulfur and do not differentiate the chemical forms of organic sulfur in coal. Solvent extraction, oxidation, and thermal degradation have been used to characterize the organic sulfur-bearing compounds in coal. These techniques generally required an alteration of the original form of the sulfur-bearing organic groups. Therefore, extracted and thermally evolved molecules may represent only a small portion of coal macromolecules (Chou et al. 1988, 1993). Although a detailed characterization of organic sulfur compounds in coal is not presently possible, the direct non-destructive x-ray absorption near edge structure (XANES) method offers great promise for group-type classification of organic sulfur in coal (Huggins et al. 1992). XANES can be used to determine Cl and organic sulfur forms simultaneously in a single sample.

In addition to Cl and sulfur, the presence of trace elements in coal is a potential concern for its future use. Utilities using Illinois coals currently are exempt from having to consider trace element emissions. However, environmental regulations eventually may limit emissions of trace elements, particularly mercury and other volatile elements.

Goals

Accurate knowledge about the fundamental associations of sulfur, Cl, and trace elements in coal is important to the successful development of any integrated or advanced coal cleaning or coal utilization processes.

The goals of this study were to use a direct and nondestructive method, XANES, to more accurately define the modes of occurrences of Cl, sulfur, and selected trace elements in as-shipped Illinois coals and to obtain data on Cl removal during fine (–200 mesh) and ultra-fine (–400 mesh) wet-grinding of coals and during froth flotation, designed primarily for the removal of pyrite and ash.

Methods and Materials

Among 34 as-shipped coal samples available for this study, 19 samples with Cl contents of 0.12 to 0.49% plus 2 other samples with lower Cl contents (0.08% and 0.02%) were selected for this study. These 21 coal samples from five geographic areas of the Illinois coal field (fig. 1) represented production of Illinois coal with low, medium, and high Cl.

A split of each coal sample was ground to –60 mesh size to be used for total sulfur and Cl analysis by ASTM procedures (ASTM 2000) and for determining forms of Cl and sulfur by XANES. A second split of each of the selected 21 coal samples was passed through a jaw crusher and then a roller crusher to reduce the particle size of the coal to < 3/8 inch and –4 mesh, respectively, for the Cl leachability tests. The Cl content in the as-shipped coals and wet-ground products was determined by ASTM methods (ASTM 2000).

The Cl x-ray absorption fine structure (XAFS) spectra for Cl were obtained at the beam-line X19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in Upton, New York, by suspending the coal samples in the monochromatic x-ray beam in ultra-thin (6-µm) polypropylene bags. All 21 samples were analyzed. The Cl XAFS spectra were collected in fluorescence geometry using a Lytle-type fluorescent detector with nitrogen as the ionization gas and helium in the sample chamber. The beam-line was operated in the focused spot mode, although the spot was placed somewhat out of focus in order to obtain better sampling of the coal. Each spectrum consisted of about 500 points collected at energies between about 50 eV below the Cl edge (2,825 eV) to about 300 eV above the edge. Dilute samples of sodium chloride in boric acid were used as the primary standards for the Cl edges. The principal peak position of the derivative XANES spectrum of sodium chloride was defined as the zero point of energy, taken by definition as 2,825 eV, for the purpose of calibrating the Cl XANES spectra. All spectra were collected and stored on a MicroVAX computer at NSLS and then transferred electronically to a similar computer at the University of Kentucky for analysis.

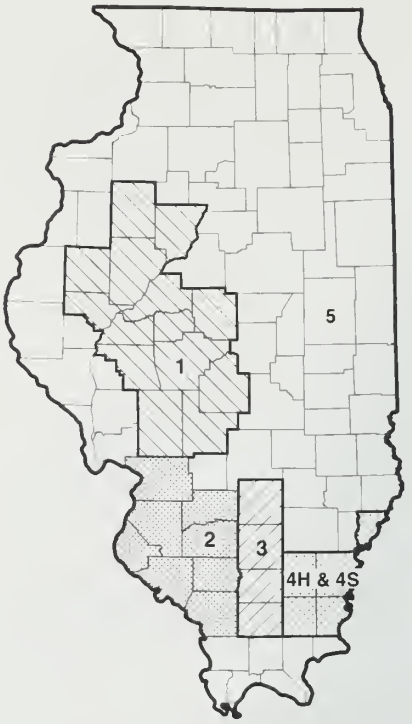

Figure 1 Map of the five Illinois coal regions where as-shipped samples were collected. 4S refers to Springfield Coal seam, and 4H refers to Herrin Coal seam in Region 4 (from Demir et al. 1995).

To determine the effect of froth flotation on the removal of Cl from coal, each of the 21 samples were first wet-ground to –200 mesh size. Splits of four of these 21 samples were then wet-ground to –400 mesh size. To achieve the –200 mesh particle size, about 700 g of each –4-mesh coal sample was mixed with 700 mL of cold tap water and ground in a rod mill for 30 minutes. The coal slurry was filtered and then air-dried. To achieve the –400-mesh particle size, about 700 g of each –4-mesh coal was mixed with 700 mL of cold water and ground in a rod mill for 60 minutes. The coal slurry was filtered and air-dried. Subsamples of the filter cakes were tested for particle-size distribution and for total Cl content.

Then 300 g of the 25 samples were subjected to a froth flotation and Cl release (FF/CR) procedure (fig. 2). Kerosene (0.8 to 1.0 mL) and 2-ethylhexanol (2-Et) (0.4 mL) were added in the first

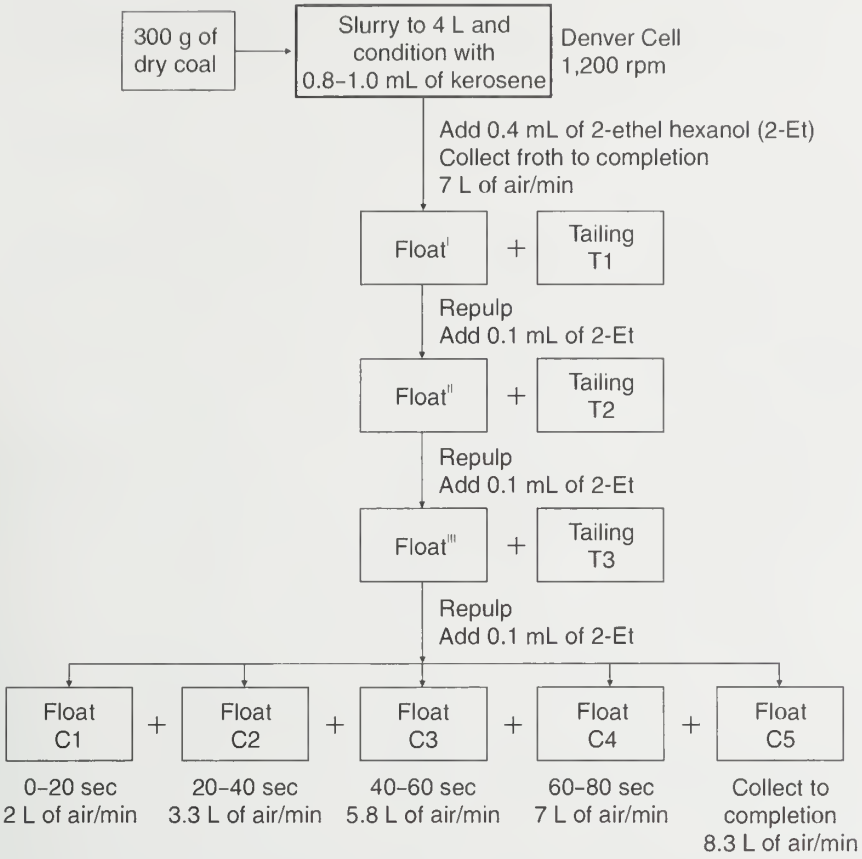

Figure 2 Froth flotation and Cl release analysis procedure.

separation of the FF/CR procedures. In subsequent separations, only 0.1 mL of 2-Et was used. The clean concentrates (floats) from each FF/CR test were combined to obtain a composite product that contained 80% of the total combustibles in the feed as described by Demir et al. (1995).

The effect of water temperature on Cl release during wet-grinding was evaluated for one of the samples (C-32661). That sample was ground to –200 mesh and to –400 mesh using the same steps as for cold water wet-grinding. The initial temperature of the hot water in the rod mill was 81°C, and the final was 57°C for the –200 mesh test. For the –400 mesh test, the initial temperature of the hot water in the rod mill was 75°C, and the final temperature was 47°C.

Products obtained from the FF/CR procedure and from hot-water grinding were analyzed for ash, Cl, forms of Cl (by XANES), Na, K, surface area, and pore volume. The surface area and pore volume data were obtained using nitrogen gas sorption at 77°K.

A XANES procedure for the quantification of different forms of Cl, similar to that for sulfur, has not been established because most coals appear to have only one major form of Cl. Five Illinois coals, each from a different geographic region (fig. 1), were heated to 125°C for 24 hours under nitrogen to separate the more volatile Cl from the less volatile Cl in the coals. The Cl XANES spectra for the five coals, before and after heating, were then compared.

Sulfur XAFS spectra also were obtained at the beam-line X-19A at NSLS, Brookhaven National Laboratory. The same procedure as described for Cl XANES analysis was used, but dilute samples of elemental sulfur were the primary standards for the sulfur edges. The principal peak position of the elemental sulfur XANES spectrum (2,472 eV) was defined as the zero point of energy for the purpose of calibrating the sulfur XANES spectra. Sulfur XANES spectra were obtained for all 21 test coals.

Sulfur XANES spectra from the coal samples were used as input to a least squares fitting program (EDGFIT) that interactively fits a set of Lorentzian-Gaussian shaped peaks and an arc tangent step function to the spectral region between –8 eV and +16 eV. A standardized procedure first fitted a highly constrained description of the peaks and step function to the data and then progressively removed the constraints as the overall fit came increasingly closer to the data. The initial input parameters and the least squares fitting procedure were developed empirically over the last four years. The final output of the algorithm listed the positions and areas of the peaks. The identity and approximate percentage of sulfur in each form were derived, respectively, from the peak positions and areas, obtained through the least squares fitting. As has been shown previously (Huffman et al. 1994, Huggins et al.1993b), the position of the peak reflects the valence state of the form of sulfur and increases in the order: pyrrhotite (–2.0 eV), pyrite (–0.6 eV), elemental sulfur (0.0 eV), aliphatic sulfide (0.7 eV), thiophene derivatives (1.4 eV), sulfoxide (3.5 eV), sulfone (8.0 eV), sulfonate (9.0 eV), and sulfate (10.2 eV). As discussed in detail elsewhere (Huggins et al. 1993b), the pyritic sulfur cannot be adequately determined by this method, and we recommend that an alternatively determined value be used in place of the XAFS-determined pyritic sulfur. Once a more accurate value has been determined, the remaining sulfur in the coal can be subdivided among the non-pyritic forms with an accuracy of about ±10%, according to the XANES results.

The XAFS spectroscopy is an advanced, direct, and nondestructive synchrotron-based assessment technique. We tested the usefulness of this technique for determining the forms and associations of trace elements in Illinois coal samples. If more accurate information is obtainable from a direct non-destructive technique, that information would help in designing a more effective physical coal cleaning process in as-shipped Illinois coal samples.

The XAFS spectra obtained from different elements in each coal sample were divided into two separate regions: the XANES region and the extended XAFS (EXAFS) region. The XANES region was used directly as a fingerprint, whereas the EXAFS region was mathematically manipulated further to obtain a radial structure function, which provided information on the coordination environment of the element. For trace elements, the EXAFS structure is useful only if the element is somewhat concentrated (>50 mg/kg) or surrounded by heavy elements. Because of this complication and others, our interpretations of the elemental modes of occurrence were based solely on the XANES region in most instances.

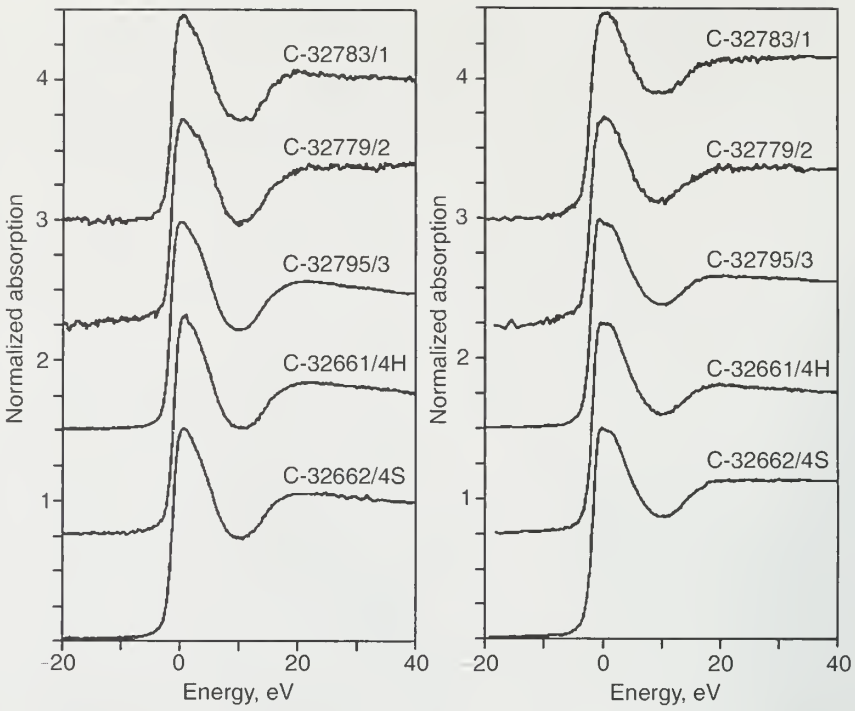

Figure 3 XANES spectra of Illinois coals from the five different geographic regions before (left) and after (right) heat treatment.

Results and Discussion

Cl XANES Analysis

The Cl XANES spectra for the 21 coals were similar, and anionic chloride was determined to be the predominant form of Cl present. The identity of the positive counter ions associated with the chloride in the coals could not be unambiguously determined from XANES spectra, lending support to previous interpretations (Demir et al. 1990, Chou 1991) that most of the Cl in Illinois coals is adsorbed on the walls of micropores in coal macerals in an exchangeable ionic form, or as Na^+ and Cl^- ions dissolved in pore water.

The Cl XANES spectra for five coals, before and after mild heating at 125°C for 24 hours in a nitrogen atmosphere (fig. 3) show some subtle differences between the two sets: (1) the shape of the main peak becomes less pointed at its apex upon heating, and (2) the rise from the minimum at about 10 to 20 eV is much more pronounced in the spectra of the original samples than in spectra of the samples after heating. These differences may mean that the chloride ions have lost some of the water molecules in their coordination sphere (Huggins and Huffman 1995).

Sulfur XANES Analysis

The sulfur XANES spectra of the 21 coal samples showed noticeable differences (table 1). The sulfur XANES spectra of three samples (C-32782, C-32665, and C-32776) were unintentionally recorded twice, and the least squares fitting of these duplicate spectra was completed before we realized they were duplicates. These duplicate spectra provided a reassuring test of the reproducibility of the least squares fitting analysis procedure.

The sulfur XANES data (table 1) show that the thiophenic sulfur accounts for a major portion (61 to 82%) of the total organic sulfur in coals. However, there are notable variations among the coal samples, which appear to be related to sample location. Coal samples from regions 3, 4H, and 4S are located in a deeper part of the Illinois Basin than samples from regions 1 and 2. As shown in table 1, the amount of thiophenic sulfur with respect to total organic sulfur for samples from regions 1 and 2 range from 61 to 65%, whereas the samples from the other regions range from 64 to 82%. Based on chemistry, other forms of organic sulfur can lose hydrogen and turn into a thiophenic sulfur form by heating. Coal samples in a deeper part of the Illinois Basin should have been subjected to greater heat and pressure, resulting in more carbonizations or greater coalification (Chou et al. 1991). Therefore, the greater amount of thiophenic sulfur observed in the samples from a deeper part of the Illinois Basin could be a result of their more extensive thermal experience.

Leachability of Cl

Wet-grinding the coal samples to –200 mesh decreased the Cl content of the coals of regions 1 and 3 by 17 to 67% (table 2). Grinding the coals from other regions reduced the Cl content by 5 to 38% for five of the samples; for the remaining nine samples, the Cl did not change much or appear to be enhanced, most likely because of analytical error or contamination. Wet-grinding four of the coals to –400 mesh reduced Cl contents 4% to 58%. Compared with the –200 mesh samples, grinding to –400 mesh increased Cl reduction for two of the four coals investigated (7 and 17%).

The (FF/CR) procedure further decreased the Cl content of most of the ground samples from regions 1, 2, and 3 by 14 to 60% beyond that achieved by

Table 1 Distribution of sulfur forms in selected coal samples derived from XANES analysis.

Coal	Seam[1]	% of total sulfur					
		Total sulfur[2]	Pyritic	Sulfate	Thiophenic	Organic	Thiophenic in % of organic sulfur
Region 1							
C-32777	S	3.14	22	2	47	27	64
C-32782	S	3.90	18	7	47	27	64
C-32782[3]	S	3.90	20	7	46	28	62
C-32783	H	4.41	21	9	42	27	61
Region 2							
C-32779	H	4.20	16	1	51	28	65
C-32815	H	3.73	27	4	42	25	63
Region 3							
C-32784	H	1.79	34	18	30	13	70
C-32795	H	0.73	10	12	64	14	82
C-32796	H	1.05	45	4	38	13	75
C-32801	H	1.98	38	9	37	16	70
C-32802	H	3.12	25	5	46	24	66
C-32803	H	2.54	28	6	45	21	68
Region 4H							
C-32661	H	2.89	35	8	40	16	71
C-32665	H	2.73	34	8	40	18	69
C-32665[3]	H	2.73	35	7	41	16	72
C-32776	H	3.13	29	6	42	22	66
C-32776[3]	H	3.13	33	6	39	22	64
Region 4S							
C-32662	S	1.51	35	11	43	11	80
C-32663	S	2.18	30	21	30	13	70
C-32772	S	2.38	40	7	39	14	74
C-32775	S	2.98	38	6	40	16	71
C-32780	S	3.32	26	7	47	20	70
C-32781	S	3.02	38	6	43	13	77
C-32793	S	1.64	41	10	35	14	71

[1] H, Herrin seam; S, Springfield seam.
[2] By ASTM analysis, weight percent, dry coal basis.
[3] Duplicate run.

wet-grinding alone (table 2). For one sample (C-32793) from region 4S, Cl content was further reduced by 38%; no further reduction occurred for other samples from regions 4S and 4H. The combination of wet-grinding and FF/CR procedures reduced Cl contents of most samples from regions 1, 2, and 3 by 17 to 81% and one sample from region 4S by 60%.

Grinding a Herrin (No. 6) Coal sample (C-32661) in hot water extracted no K and only small amounts of Cl and Na (table 3). Some of the extracted Cl was likely in the form of dissolved Na^+Cl^- from the pore water of the coal sample. Cold-water grinding followed by the FF/CR process removed substantial amounts of Na and K (table 3) because the flotation process removed some of the host minerals (clays) in which the great bulk of these two elements was located. Hot-water grinding to –200 mesh or the FF/CR procedure at –200 mesh did not make much difference in the Cl contents of the products relative to the original feed. Hot-water grinding to –400 mesh decreased the Cl level to the same level as was achieved by the combination of cold-water grinding to –400 mesh and the subsequent FF/CR process. Thus, the Cl content of this particular coal was decreased primarily during rigorous grinding and was unrelated to the removal of ash during the FF/CR process.

The surface areas of three raw coal samples and a set of the FF/CR processed fractions of one coal (C-32661) were analyzed to determine whether the amounts of Cl removal could be affected by the surface area of the coal samples. The results of these limited samples indicated a positive correlation between Cl removal and the surface area of the coal sample (fig. 4).

Grinding and the FF/CR process resulted in higher surface areas and pore volumes in the product coals than in the raw feed for a selected sample (C-32661). Grinding in hot water increased the surface area and pore volume as did the combination of cold-water grinding and subsequent FF/CR

Table 2 Cl content of wet-ground coal samples before and after the FF/CR procedure.

Coal	Cl (weight % dry coal)								
	Feed	−200 mesh product		FF/CR products at −200 mesh			−400 mesh product	FF/CR products at −400 mesh	
Region 1									
C-32777	0.12	0.04	(67)[1]	0.03	(75)	{25}[2]	0.05 (58)	0.03 (75)	{40}
C-32782	0.15	0.07	(53)	0.03	(80)	{57}			
C-32783	0.16	0.07	(56)	0.03	(81)	{57}			
Region 2									
C-32779	0.08	0.05	(38)	0.02	(75)	{60}			
C-32815	0.02	0.03	(−50)[3]	0.04	(−100)	{−33}			
Region 3									
C-32784	0.39	0.28	(28)	0.24	(38)	{16}			
C-32795	0.45	0.35	(22)	0.27	(40)	{23}			
C-32796	0.38	0.24	(37)	0.18	(52)	{25}			
C-32801	0.35	0.29	(17)	0.25	(28)	{14}	0.24 (28)	0.23 (34)	{8}
C-32802	0.29	0.24	(17)	0.24	(17)	{0}			
C-32803	0.32	0.24	(25)	0.25	(22)	{−4}			
Region 4H									
C-32661	0.26	0.27	(−4)	0.28	(−8)		0.25 (4)	0.21 (19)	{16}
C-32665	0.13	0.14	(−8)	0.14	(−8)				
C-35776	0.15	0.12	(20)	0.13	(20)				
Region 4S									
C-32662	0.35	0.37	(−6)	0.37	(−6)				
C-32663	0.21	0.20	(5)	0.21	(0)				
C-32772	0.24	0.26	(−8)	0.29	(−20)				
C-32775	0.17	0.22	(−29)	0.22	(−29)				
C-32780	0.21	0.19	(10)	0.18	(14)				
C-32781	0.19	0.20	(−5)	0.20	(−5)				
C-32793	0.20	0.13	(35)	0.08	(60)	{38}	0.13 (35)	0.08 (60)	{38}

[1] Parentheses indicate the percent reduction in total Cl of feed coal.
[2] Brackets indicate a further percent reduction beyond wet-grinding.
[3] − sign indicates increase in Cl content.

Table 3 Ash, Cl, Na, and K contents, surface area, and pore volume for coal sample C-32661 prepared by hot-water grinding and cold-water grinding followed by the FF/CR process.

Coal sample	Weight %				Surface area (m^2/g)			Pore volume (cm^3/g)	
	Ash	Cl	Na	K	Total	Micropore	Mesopore	Total	Micropore
Raw	8.17	0.26	0.052	0.166	5.249	0.000	5.249	0.018	0.000
Hot-water grinding									
−200 mesh	8.43	0.24	0.034	0.168	6.929	0.000	6.929	0.025	0.000
−400 mesh	8.62	0.21	0.035	0.173	7.549	0.000	7.549	0.032	0.000
Cold-water grinding and froth flotation									
−200 mesh	3.76	0.28	0.021	0.068	5.604	0.230	5.374	0.021	<0.001
−400 mesh	2.96	0.21	0.022	0.064	6.514	0.051	6.463	0.024	<0.001

(table 3). The differences in analytical results for a set of FF/CR fractions of coal C-32661 (table 4) were too small to determine whether Cl was significantly correlated with other parameters (Na, K, surface area, pore volume).

If Cl can be removed efficiently from some samples through grinding and physical cleaning, the next consideration is management options for the Cl-enriched process water. Three basic strategies for managing the Cl-rich waste water were investigated: (1) store water in a seepage-free pond, (2) inject the waste water into underground rock formations, and (3) treat the waste water by reverse osmosis to remove Cl. The results of this investigation were included in a separate report (Chou et al. 1995).

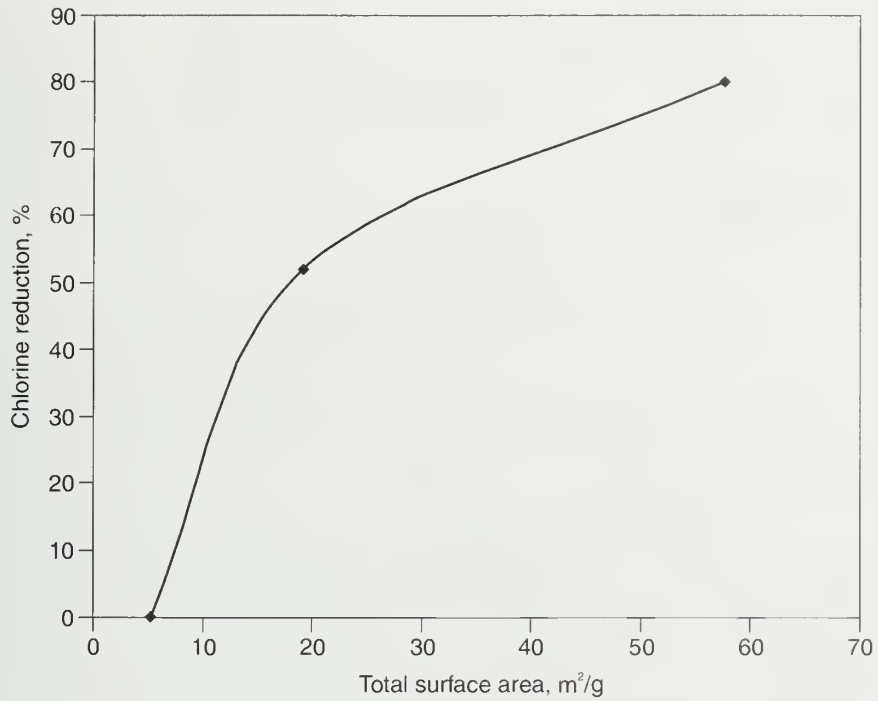

Figure 4 Correlation between total surface area and decrease in Cl content in three feed coals after wet-grinding to –200 mesh followed by froth flotation.

Trace Metal Analysis by XAFS/XANES

Several tests were performed to evaluate which trace elements could successfully be examined by the XAFS/XANES technique to determine their mode of occurrence (organic/inorganic affinity) in the coal. Using previously determined average concentrations of trace elements (Demir et al. 1994) as a guide, a sample of the Illinois Herrin (No. 6) Coal (C-32778) was chosen for this study. The XAFS/XANES spectra were interpreted by comparing them to the spectra of standard compounds. The Ti and Mn XAFS spectra of the Argonne No. 3 coal sample [Illinois Herrin (No. 6) Coal] from the Argonne Premium Coal Sample Bank and the Zn XAFS spectra of coals previously studied (unpublished XAFS data, University of Kentucky) were compared with those for the Illinois Herrin (No. 6) Coal in this study.

Arsenic The As XANES spectra were obtained for both fresh and extensively oxidized samples of Illinois coal (fig. 5). Oxidized samples were obtained by exposure to room air. In both spectra, two distinct peaks were observed, indicating the presence of two different forms of As in these samples. The peak to the negative side of 0 eV arose from As in pyrite (FeS_2), whereas the higher energy peak arose from an arsenate (AsO_4^{3-}) phase formed by oxidation of the As in pyrite (Huggins et al. 1993a, Huffman et al. 1994). These assignments were confirmed by examining the radial structure function derived

Table 4 Ash, Cl, Na, K, and combustible contents, and surface area and pore volume of fractions obtained from the FF/CR treatment of coal C-32661 ground to –400 mesh in cold water.

FF/CR	Weight %					Surface area (m^2/g)			Pore volume (cm^3/g)		
product[1]	Ash	Combustible[2]	Cl	Na	K	Total	Micropore	Mesopore	Total	Micropore	Weight fraction
C1	2.46	92.10	0.22	0.020	0.053	6.46	0.000	6.455	0.026	0.000	0.10
C2	2.63	91.66	0.23	0.023	0.058	6.64	0.000	6.637	0.021	0.000	0.15
C3	2.76	90.40	0.24	0.021	0.060	6.22	0.000	6.217	0.021	0.000	0.18
C4	2.88	91.37	0.19	0.021	0.063	6.36	0.277	6.080	0.022	0.000	0.14
C5	3.67	90.70	0.19	0.021	0.080	6.82	0.000	6.822	0.028	0.000	0.20
Tailings	25.00	71.39	0.18	0.060	0.492	8.47	0.000	8.474	0.043	0.000	0.24

[1] C, concentrate.
[2] Combustible, 100 – (% moisture + % ash).

from the EXAFS region. Although the noise level was high for the As XAFS spectrum of this sample, radial structure function for the two spectra did correctly locate the major peak for the dominant forms at about 2.05 Å for arsenic in pyrite and at about 1.30 Å for the arsenate anion (fig. 6).

Zinc The Zn spectrum in the Illinois coal sample (fig. 7) was strong and was clearly derived largely from ZnS. The RSF derived from the EXAFS region for Zn was similar to that of a ZnS standard (not shown).

Titanium The Ti spectrum of the Illinois coal had a relatively weak pre-edge peak at about 3 eV and a broad main peak between 20 and 30 eV that consisted of two components (fig. 8). The form of Ti has not yet been positively identified. This spectrum was very similar to that for Ti in the Argonne No. 3 sample and for the Ti in cleaned coal fractions from the Kentucky No. 9 seam that had been examined previously (Huggins and Huffman 1996, Huggins et al. 1997; unpublished XAFS database of the University of Kentucky). Also, because no sharp minor features were discernible in the spectrum, and because the small pre-edge peak did not exhibit any apparent splitting, virtually all of the common Ti-bearing minerals (e.g., rutile, anatase, sphene, Ti-illite) can be eliminated as being major contributors to this spectrum. Our conclusion is that such a spectrum most likely represents nanoparticles or amorphous small particles of titanium oxide that are associated with coal macerals.

Vanadium The University of Kentucky has only a limited database from which to interpret the V XAFS/XANES spectrum obtained from the Illinois seam; however, V XAFS spectra have been obtained from a sample of the Kentucky No. 9 seam by Huggins et al. (1997) and from a V-enriched fraction of the same seam by Maylotte et al. (1981a, b). The spectrum of the Illinois coal sample (fig. 9) has a sharp pre-edge feature at about 4 eV, which is indicative of either a highly distorted V^{3+} environment or an unusual V^{4+} compound. This feature is followed by two broad peaks from 10 to 30 eV. The spectrum of the Illinois coal sample for

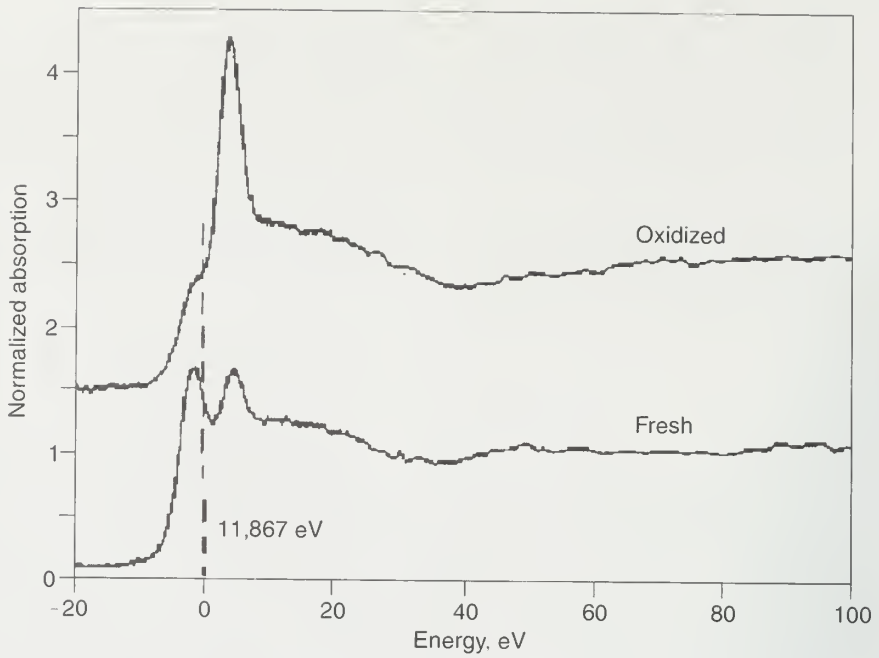

Figure 5 As XANES spectra of fresh and oxidized samples of the Illinois coal.

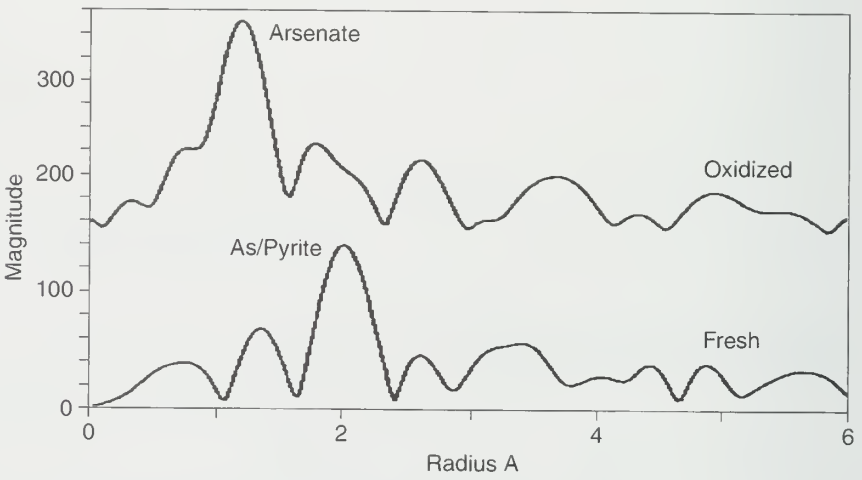

Figure 6 Radial structure functions of the As EXANES spectra for fresh and oxidized samples of the Illinois coal.

V is similar to the reported spectra of float fractions of the Kentucky No. 9 Coal sample (Maylotte et al. 1981a, b; Huggins et al. 1997).

Chromium A very weak pre-edge peak at about 2 eV above the K-edge calibration zero point indicates that all (>95%) of the Cr in the Illinois coal was present as Cr^{3+}; there was no evidence of the more toxic Cr^{6+} oxidation state (fig. 10), which, if present, would have been indicated by a much more intense peak that occurs at 4 eV. The detection limit for this technique is about 5% for Cr^{6+}. The Cr spectrum for the Illinois coal sample is similar to those for Cr in most bituminous coals (Huggins et al. 1993a, Huffman et al. 1994, Huggins and Huffman 1996). This spectrum of the Illinois coal was tentatively identified as being derived predominantly from a small-particle chromium oxyhydroxide (CrOOH) phase.

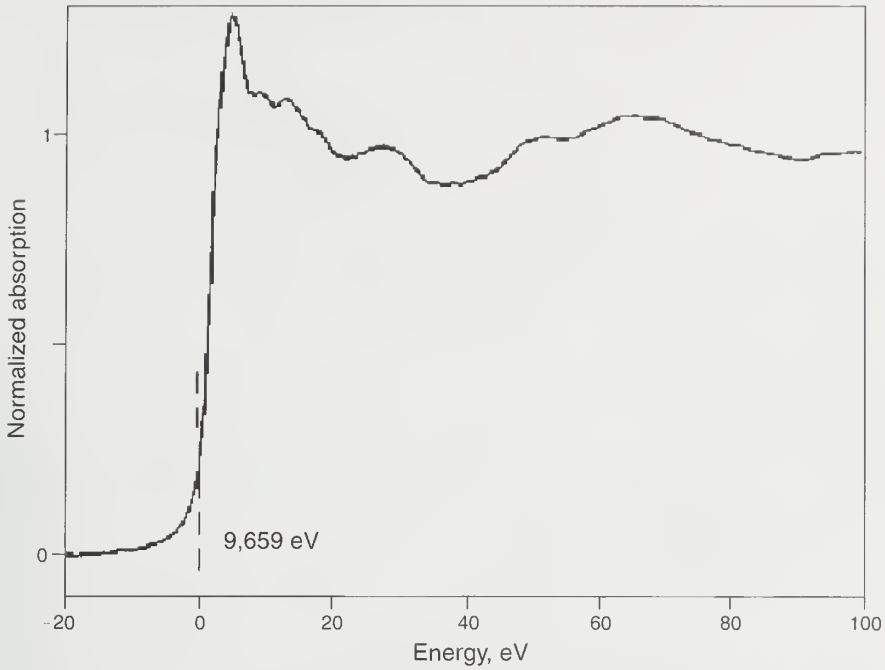

Figure 7 Zn XANES spectrum of the Illinois coal sample.

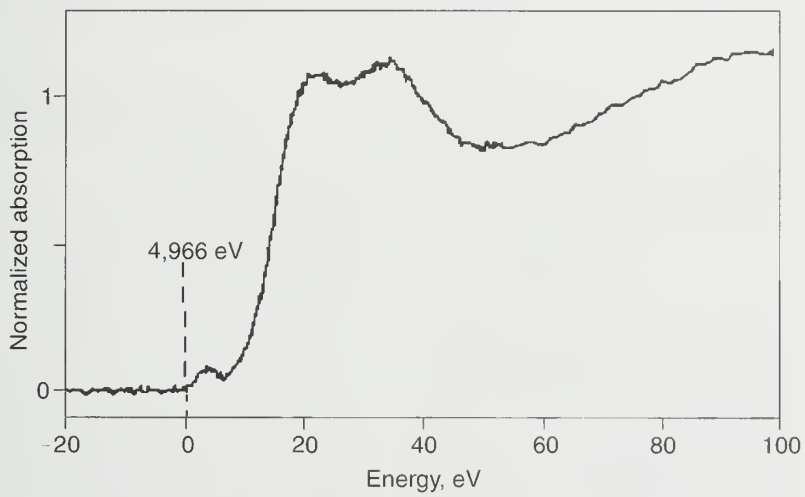

Figure 8 Ti XANES spectrum of the Illinois coal sample.

Manganese The Mn spectrum from the Illinois coal sample used in this study (fig. 11) was quite different from that from the Argonne No. 3 sample (XAFS database at the University of Kentucky). Except for a weak feature at about 17 eV, the Mn spectrum appeared to have a profile that was more similar to that of the Mn in a lignite from Beulah, North Dakota (XAFS database at the University of Kentucky). Further study using simulated Mn XAFS spectra in calcite, in illite, and in carboxyl forms showed that the observed spectrum could be well duplicated from Mn in these forms.

In summary, for some of the elements examined, such as As and Zn, the present XAFS data provide a definitive interpretation of their dominant mode of occurrence in the specific sample of Illinois coal (C-32778) investigated. For the other elements (Ti, V, Cr, Mn), the database of XAFS spectra for trace elements in coal is still too limited to allow a definitive interpretation; however, the data obtained for these elements are sufficient to rule out many of the mineralogical possibilities that have been suggested previously (Swaine 1990).

Conclusions

The Cl XANES spectra were similiar for 21 coal samples from five different coal-producing regions. The chloride anion was the predominant form of Cl present. The identity of the positive counter ions with which the chloride anion was associated in the coals could not be unambiguously determined from the XANES spectra.

Sulfur XANES data indicated that oxidized organic sulfur and elemental sulfur, if present, were relatively minor components of the Illinois coals studied. The ratios of thiophenic sulfur to total organic sulfur varied with sample location (region). For samples from western and southwestern regions of the Illinois coal field, the ratios ranged from 0.61 to 0.65; for the southern and southeastern regions, the ratios were in the range of 0.64 to 0.82.

Wet-grinding of coal samples from regions 1 and 3 to –200 mesh decreased their Cl contents by 17 to 67%. For other regions, only 5 of the 12 samples lost Cl (5 to 38%) during wet-grinding to –200 mesh. Wet-grinding of four selected coals to –400 mesh decreased their Cl contents (4 to 58%). Compared with the –200 mesh samples, wet-grinding to –400 mesh yielded improvement in Cl removal (7 and 17%) for two of the four coals.

The FF/CR procedure further decreased the Cl content in most of the –200-mesh samples from regions 1, 2, and 3 by 14 to 60%. For one sample from region 4S, Cl content decreased 38%. Other samples from region 4S and region 4H showed no further reduction. The results also indicated that a combination of wet-grinding and FF decreased the Cl content in most samples from regions 1, 2, and 3 by 17 to 81% and in one sample from region 4S by 60%. The Cl content in coal can

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be decreased primarily during rigorous grinding, regardless of whether the initial water temperature is hot or cold.

For the three coal samples examined, Cl removal increased as surface area increased. Conversely, for a set of FF/CR fractions of one of the three coal samples, Cl removal was not correlated with changes in surface area and other parameters such as Na and K contents and pore volume.

XANES data of selected trace elements provided a definitive interpretation of the predominant modes of occurrences of As and Zn in a sample of Illinois Herrin (No. 6) Coal. For the other elements (Ti, V, Cr, Mn), the database is still too limited to allow a definitive interpretation; however, the data obtained on these elements were sufficient to rule out many of the minerals that have been suggested by other workers.

A study of stepwise heating of coal in an attempt to remove the more volatile Cl step by step from the less volatile Cl and to examine the residues (char) by XANES is recommended for Illinois coals and other coals. Such a study may provide additional insight about the nature of Cl in coal. Also, additional investigations using in situ techniques are needed to determine volatile alkali metals and Cl-containing compounds produced during coal combustion. Data from such investigations ought to help explain the different corrosion problems of utility boilers that use different coals, such as Illinois coals versus British coals.

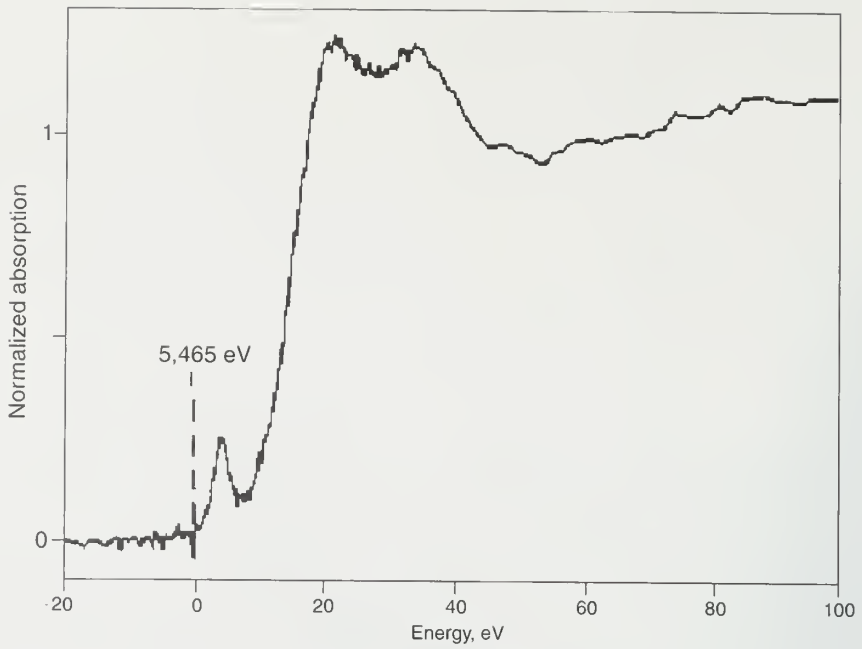

Figure 9 V XANES spectrum of the Illinois coal sample.

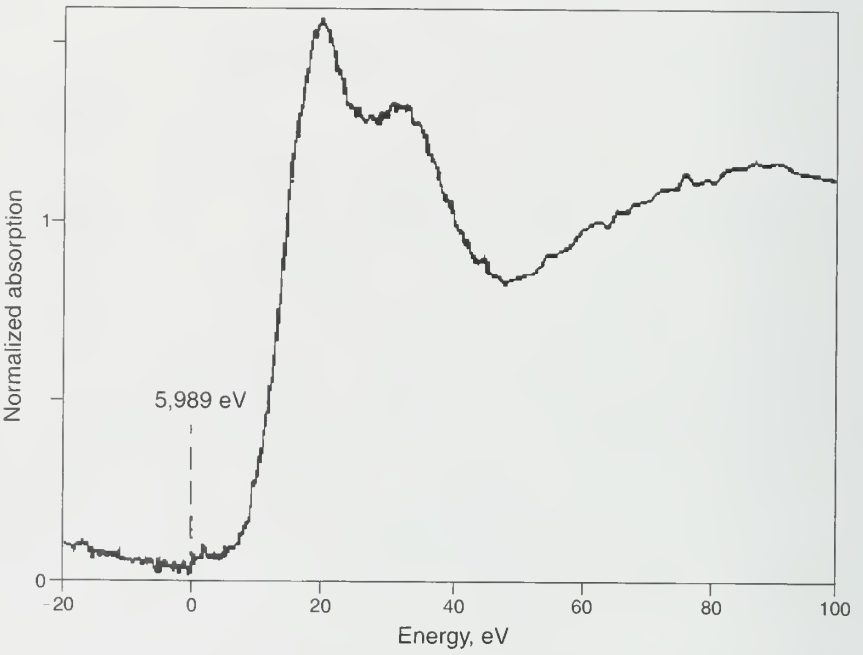

Figure 10 Cr XANES spectrum of the Illinois coal sample.

Acknowledgments

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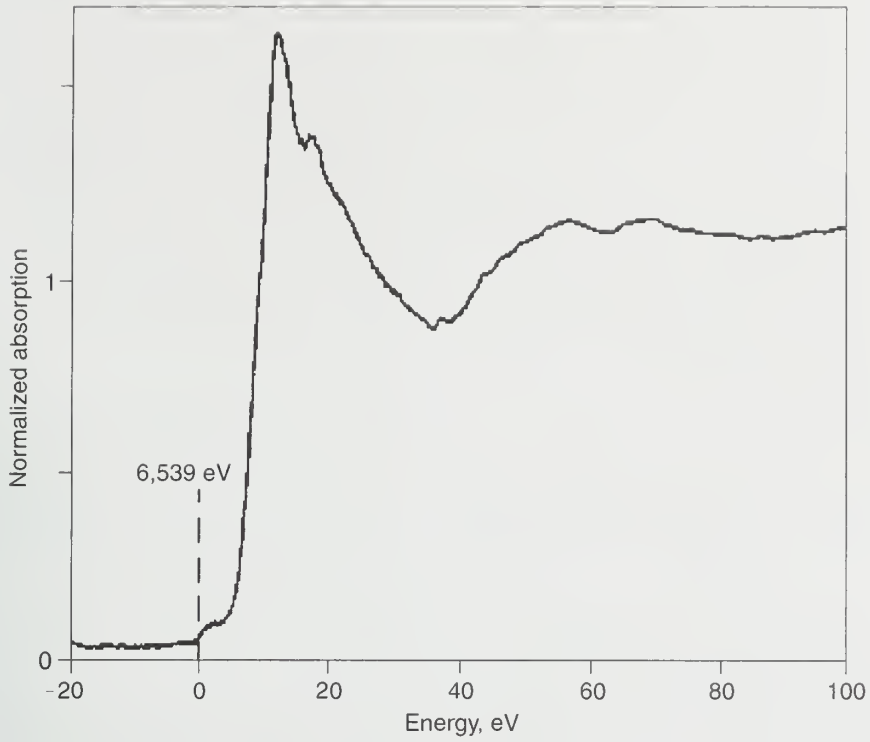

Figure 11 Mn XANES spectrum of the Illinois coal sample.

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